

Synthesis and study of olefin metathesis catalysts supported by redox-switchable diaminocarbene[3]-ferrocenophanest

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A redox-switchable ligand, *N,N'*-dimethyldiaminocarbene[3]ferrocenophane (**5**), was synthesized and incorporated into a series of Ir- and Ru-based complexes. Electrochemical and spectroscopic analyses of (**5**)Ir(CO)₂Cl (**15**) revealed that **5** displayed a Tolman electronic parameter value of 2050 cm⁻¹ in the neutral state and 2061 cm⁻¹ upon oxidation. Moreover, inspection of X-ray crystallography data recorded for (**5**)Ir(*cis,cis*-1,5-cyclooctadiene)Cl (**13**) revealed that **5** was sterically less bulky (%V_{Bur} = 28.4) than other known diaminocarbene[3]ferrocenophanes, which facilitated the synthesis of (**5**)(PPh₃)Cl₂Ru-(3-phenylindenylid-1-ene) (**18**). Complex **18** exhibited quasi-reversible electrochemical processes at 0.79 and 0.98 V relative to SCE, which were assigned to the Fe and Ru centers in the complex, respectively, based on UV-vis and electron pair resonance spectroscopic measurements. Adding 2,3-dichloro-5,6-dicyanoquinone over the course of a ring-opening metathesis polymerization of *cis,cis*-1,5-cyclooctadiene catalyzed by **18** ([monomer]₀/[**18**]₀ = 2500) reduced the corresponding rate constant of the reaction by over an order of magnitude (pre-oxidation: *k*_{obs} = 0.045 s⁻¹; post-oxidation: *k*_{obs} = 0.0012 s⁻¹). Subsequent reduction of the oxidized species using decamethylferrocene restored catalytic activity (post-reduction: *k*_{obs} = up to 0.016 s⁻¹, depending on when the reductant was added). The difference in the polymerization rates was attributed to the relative donating ability of the redox-active ligand (*i.e.*, strongly donating **5** versus weakly donating **5**⁺) which ultimately governed the activity displayed by the corresponding catalyst.

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Introduction

Redox-switchable catalysis¹ uses oxidation state changes to modulate catalytic activity. A recent example was reported by Matyjaszewski who demonstrated electrochemical control over an atom transfer radical polymerization reaction by regulating a Cu^I/Cu^{II} couple.² However, formally changing the oxidation state of metal centers can result in irreversible degradation or a loss in the desired catalytic activity due to coordination sphere variation. As such, attention has been directed toward the development of redox-switchable ligands as transition metal catalysts are typically sensitive to minute differences in ligand donorities.³

Redox-switchable ligands offer a means to impart unique selectivities and/or activities to supported catalysts through oxidation state changes and, in many cases, may be switched using chemical or electrochemical processes.^{4,5} A seminal example was reported by Wrighton in 1995,⁴ where it was shown that a 1,1'-bis(diphenylphosphino)cobaltocene Rh complex (Fig. 1) facilitated hydrosilations or hydrogenations

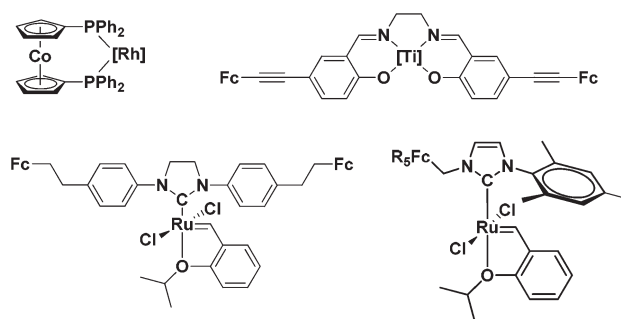


Fig. 1 Representative examples of various complexes containing redox-switchable metallocenes. Fc = ferrocenyl.^{4,5c,7a,24} Ph = phenyl. R = hydrogen or methyl.

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† Electronic supplementary information (ESI) available: Additional synthetic procedures, discussions of additional FcDAC-Ru complexes, NMR spectra, EPR spectra, cyclic voltammograms, and X-ray data (PDF). CCDC 938913, 938914, 938915, 938916 and 938917. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51278a

depending on the oxidation state of the redox active ligand (*i.e.*, cobaltocene *versus* cobaltocenium). Gibson and Long later showed that the rate of the ring opening polymerization (ROP) of lactide was dependent on the oxidation state of a ferrocene unit contained within a *N,N'*-ethylenebis(salicylimine) supported Ti catalyst.^{5c} The use of ferrocene containing ligands to vary the rate of ROP reactions has since been elegantly expanded by Diaconescu⁶ to include complexes of Y, In, and Ce. Similarly, ferrocene-containing ligands have been utilized⁷ by Plenio^{7a} and Wang^{7b} as “phase tags”, for Ru-based olefin metathesis catalysts,⁸ whereby ligand oxidation drives a change in solubility and facilitates catalyst recovery. Plenio also reported efforts toward using ligand oxidation as a means to bias the intrinsic *E:Z* selectivities displayed by a Ru catalyst containing a ligand bearing pendant ferrocenyl substituents.⁹

Although a handful of redox-switchable ligands have been studied,^{10,11} their utility in controlling catalytic reactions is still rather limited.^{5–7,12,13} This deficiency may be, at least partially, due to the fact that many of the aforementioned ligands are bi- or multi-dentate, which confines their range of possible geometries and catalytically active transition metal complexes into which they may be incorporated. One solution to this limitation may be found within the *N*-heterocyclic carbenes (NHCs),¹⁴ which are a class of ligands finding tremendous utility in catalysis.¹⁵ As strong σ -donors,¹⁶ they coordinate numerous metals in a range of oxidation states and do so in a monodentate fashion.^{15,17} Furthermore, compared to their phosphine counterparts, they often impart enhanced stability and/or catalytic activity upon coordination to a transition metal.¹⁸ In light of these advantages, we have launched a program to explore redox-active NHCs as a general class of ligands for bestowing redox-switchable functions onto a broad range of transition metals.^{19–24} For example, we recently disclosed a series of redox-switchable Ru-based olefin metathesis catalysts bearing *N*-ferrocenylated NHCs (Fig. 1).²⁴ The activities displayed these catalysts in ring-closing metathesis reactions were found to depend upon the oxidation state of the redox-active ligand: catalysts supported by ferrocenium containing NHCs were significantly less active than their neutral analogues, which was attributed to the relative donating abilities of the respective ligands.

Previously, we¹⁹ and others²⁵ reported the diaminocarbene-[3]ferrocenophanes (FcDACs; Fig. 2)²⁶ as a new class of redox-switchable ligands. The extent to which the associated redox processes impacted metals coordinated to the FcDACs were measured by analyzing $[(L)M(CO)_2Cl]$ (*M* = Rh or Ir) type

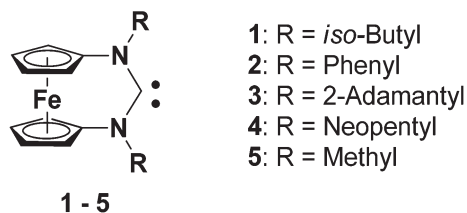


Fig. 2 Structures of various *N,N'*-diaminocarbene[3]ferrocenophanes.^{19,25}

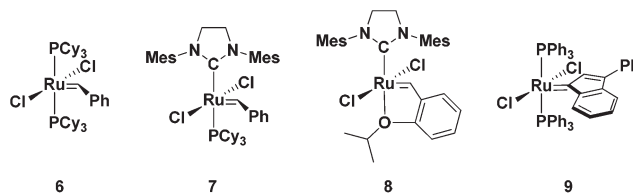


Fig. 3 Structure of various Ru based olefin metathesis catalysts. Mes = 2,4,6-trimethylphenyl. Ph = phenyl. Cy = cyclohexyl.

complexes using IR spectroscopy, since the stretching frequencies displayed by the carbonyl groups are sensitive to the other ligands.²⁷ Indeed, the ν_{CO} s displayed by these complexes were measured to hypsochromically shift by 13–21 cm^{-1} upon oxidation of the FcDAC ligand.^{19,20}

Building on these results, we sought to investigate the ability of the FcDAC ligands to impart redox-switchable functions to catalytically-active transition metals and to facilitate comparisons to other redox-switchable catalysts containing ferrocene moieties. Attention was directed toward catalysts used to facilitate olefin metathesis, as this is a powerful reaction that has been used for the synthesis of small molecules as well as macromolecular materials.²⁸ In particular, Ru-based catalysts have garnered much success due to their high stabilities toward oxygen, moisture, and a broad range of functional groups.²⁹ Moreover, NHCs have played a prominent role in establishing the utility of Ru-based metathesis catalysts, as they often enhance activity and/or stability relative to other ligands, particularly phosphines.^{18a,30,31} Representative examples of various Ru-based catalysts which have found widespread use in a variety of olefin metathesis reactions are shown in Fig. 3 (6–8).^{28b,32,33} Herein, we describe the synthesis and study of Ru-based olefin metathesis catalysts supported by redox-switchable FcDAC ligands.³⁴

Results and discussion

Attempted synthesis of Ru complexes containing 1 or 2

We first attempted to synthesize $(1)(PCy_3)_2Cl_2Ru=CHPh$ as an analogue to the Grubbs second generation catalyst (7). Although the respective free diaminocarbene (*i.e.*, 1) could not be isolated,³⁵ *in situ* deprotonation of the known¹⁹ salt $[1H][BF_4]$ using NaHMDS (HMDS = hexamethyldisilazane) followed by the addition of 6 appeared to result in the formation of the desired complex, as evidenced by diagnostic signals in the 1H and ^{31}P NMR spectra recorded for the crude reaction mixture (Fig. 4). For example, a new 1H NMR signal attributed to the benzyldene proton was observed at 20.1 ppm (d, 1H, $J = 6.3$ Hz) and a ^{31}P NMR signal had appeared along with liberated PCy_3 (28.5 ppm and 12.3 ppm, respectively) ($CDCl_3$). Unfortunately, attempts to isolate $(1)(PCy_3)_2Cl_2Ru=CHPh$ were unsuccessful, presumably due to its low stability in solution, even in the absence of air and moisture.³⁶ Attempts to deprotonate $[2H][BF_4]$ in the presence of 6 under various conditions also resulted in decomposition.

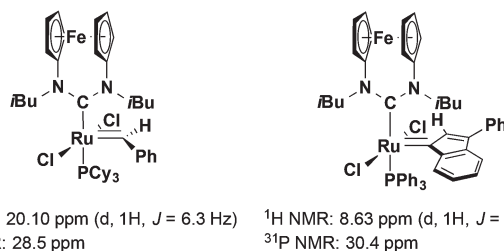
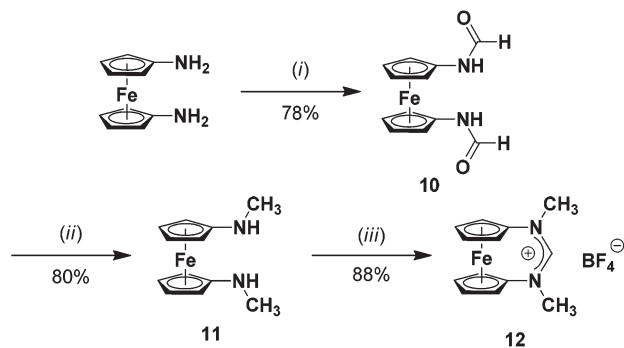


Fig. 4 Diagnostic signals observed in the ^1H and ^{31}P NMR spectra recorded for (1)(PCy₃)Cl₂Ru=CHPh and (1)(PPh₃)Cl₂Ru=(3-phenylindenylid-1-ene) in CDCl₃.

We reasoned that the instability of (1)(PCy₃)Cl₂Ru=CHPh may be due to dissociation of the bulky phosphine ligand which renders the corresponding coordinatively unsaturated Ru complex susceptible to decomposition.^{28e,37} Subsequent efforts were directed toward the Ru indenylidenes,^{31f,33,38,39} as such complexes have gained attention for their high thermal stabilities and high activities in various olefin metathesis reactions.⁴⁰ We surmised that decreasing the steric bulk of the phosphine from PCy₃ to PPh₃ would also improve the stability of the resulting complex.⁴¹ *In situ* deprotonation of [1H][BF₄] followed by the addition of (PPh₃)₂Cl₂Ru=(3-phenylindenylid-1-ene) (9) appeared to form the desired complex as determined by NMR spectroscopic analysis of the crude reaction mixture. Diagnostic ^1H and ^{31}P signals were observed at $\delta = 8.63$ (d, 1H, $J = 7.2$) and 30.44 ppm (CDCl₃), respectively, which compared well to those observed for previously reported indenylidene complexes containing NHCs (^1H : 8.31–7.01 (d, $J = 7.7$ –7.2) and ^{31}P : 30.51–27.3 ppm).^{38,40e,g} Additionally, free PPh₃ was observed at -4.3 ppm. Although small quantities of (1)(PPh₃)Cl₂Ru=(3-phenylindenylid-1-ene) were isolated, we were unable to access enough material for further investigation, even after exploring a variety of purification techniques (*e.g.*, precipitation, trituration and column chromatography). Unfortunately, attempts to synthesize phosphine-free complexes containing 1, such as (1)Cl₂Ru=CH(2-iso-propoxy-Ph)⁴² or (1)(SIMes)Cl₂Ru=CHPh,^{3c,43,44} (SIMes = 1,3-dimesitylimidazol-2-ylidene) were also unsuccessful.

Synthesis and study of *N*-methyl FcDAC 5 and its transition metal complexes

Although bulky *N*-substituents can often enhance the stability of Ru catalysts due to steric protection of the metal center, they may also hinder coordination in some cases. For example, attempts to prepare Ru complexes containing the bulky acyclic diaminocarbenes (ADCs), 1,3-di(1-adamantyl)-4-dihydroimidazol-2-ylidene or bis(iso-propylamino)-formamidin-2-ylidene were reported to be unsuccessful.^{45,46} Although FcDACs feature N–C–N bond angles that are comparable to those displayed by the ADCs (approximately 120°),^{25,47} a stable ADC–Ru complex, *N,N'*-dimesityl-*N,N'*-dimethylformamidin-2-ylidene)-(SIMes)Cl₂Ru=CHPh, was synthesized and found to adopt a conformation where both *N*-methyl substituents were oriented towards the coordinated Ru center.^{43b} Thus, we hypothesized



Scheme 1 Synthesis of **12**. (i) Phenyl formate (2.2 equiv.). (ii) (a) LiAlH₄ (5 equiv.), THF, 0 °C → reflux, 1 h; (b) H₂O. (iii) HBF₄, (MeO)₃CH, 60 °C, 30 min.

that an FcDAC bearing *N*-methyl substituents may enable isolation of a stable Ru complex supported by this ligand.

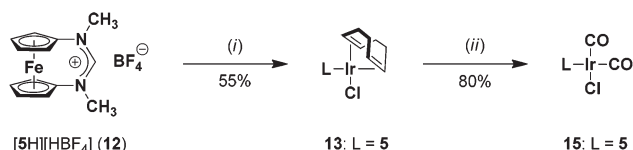
As summarized in Scheme 1, the synthesis of [5H][BF₄] (**12**) began with 1,1'-diaminoferrrocene which was formylated with phenyl formate to give *N,N'*-diformamidoferrocene **10**. Treatment of **10** with LiAlH₄ followed by an aqueous workup yielded *N,N'*-dimethylaminoferrocene **11**, which was formylatively cyclized with trimethylorthoformate in the presence HBF₄ to give **12**. The diagnostic ^1H NMR signal attributed to the C2 proton of this salt was observed at 8.71 ppm (DMSO-*d*₆) and was in good agreement with that previously recorded for [1H][BF₄] (8.80 ppm, DMSO-*d*₆). The solid state structure of **12** was elucidated by growing single crystals suitable for X-ray diffraction analysis *via* slow diffusion of diethyl ether into a saturated CH₂Cl₂ solution (Fig. S16†). The N–C–N bond angle (129.4(3)°) measured in the solid state structure was nearly identical to that observed for [1H][BF₄] (129.6(3)°)¹⁹ and comparable to those reported for other crystalline formamidinium-[3]ferrocenophanes (129.7(2)–131.1(6)°).²⁵ Moreover, the cyclic voltammogram (CV) recorded for **12** in CH₂Cl₂ exhibited a reversible, one electron oxidation at $E_{1/2} = 1.03$ V *versus* SCE, which was assigned to the Fe center (Table 1; see also Fig. S4†). The $E_{1/2}$ value recorded for **12** is similar to those measured for [1H][BF₄] and [2H][BF₄] (1.10 V, and 1.14 V *versus* SCE, respectively) under otherwise identical conditions.¹⁹ Deprotonation of **12** using NaHMDS in C₆D₆ afforded the free carbene **5**, as evidenced by the disappearance of the signal assigned to the C2 formamidinium proton.⁴⁸ Although we were unable to isolate **5**, it was found to be sufficiently stable in solution in the absence of air and moisture to record a ^1H NMR spectrum.

Prior to incorporating **5** into an olefin metathesis catalyst, the steric and electronic parameters of this ligand were evaluated. As mentioned above, complexes of the type (L)M(COD)Cl and (L)M(CO)₂Cl (L = NHC or phosphine, M = Rh, Ir) have proven to be useful for such purposes.^{20,27} Furthermore, analogous complexes containing **1** have been previously reported, enabling subtle differences in the steric and electronic influences of the *N*-substituents to be deconvoluted.^{19,20} As shown in Scheme 2, *in situ* deprotonation of **12** using NaHMDS followed by the addition of [Ir(COD)Cl]₂ afforded **13** in 55% yield after

Table 1 Summary of electrochemical properties for various Ir and Ru complexes^a

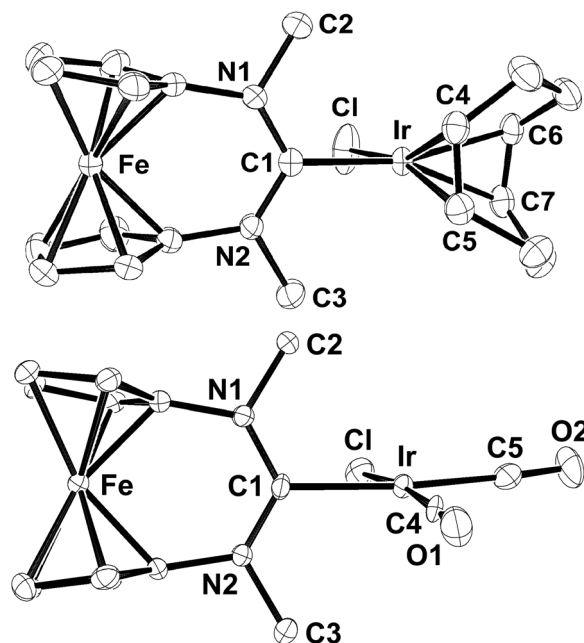
	$E_{1/2}$ ^b (V)
12	1.03
13	0.81, 1.02
15	0.96 ^c
18	0.79, 0.98
9	0.84

^a Conditions: CH₂Cl₂ solution containing 1 mM analyte and 0.1 M [Bu₄N][PF₆] as the supporting electrolyte. All redox processes were found to be reversible or quasi-reversible. ^b Values are reported relative to SCE through the addition of Fe* as an internal standard adjusted to −0.057 V. ^c The Ir-centered oxidation was not observed within the solvent window.

**Scheme 2** Synthesis of Ir(COD)Cl and Ir(CO)₂Cl complexes containing **5**. (i) (a) NaHMDS (1.0 equiv.), toluene, rt, 5 min; (b) [Ir(COD)Cl]₂ (0.5 equiv.), toluene, rt, 12 h. (ii) CO (1 atm), CH₂Cl₂, rt, 3 h. rt = room temperature.

isolation *via* column chromatography (media: SiO₂; eluent: 3 : 1 v/v hexanes–ethyl acetate). The ¹³C NMR chemical shift assigned to the 2-position of **5** in **13** was observed at 215.6 ppm in CDCl₃, similar to that previously reported for (1)Ir(COD)Cl (**14**) (213.2 ppm).²⁰ The corresponding carbonyl complex (5)Ir(CO)₂Cl (**15**) was obtained upon stirring a CH₂Cl₂ solution of **13** under an atmosphere of CO. The IR spectrum of **15** (CH₂Cl₂) displayed ν_{CO} at 2065 and 1983 cm^{−1}, similar to those previously recorded for (1)Ir(CO)₂Cl (**16**) (ν_{CO} = 2062 and 1982 cm^{−1}).²⁰

The solid state structures of **13** and **15** were elucidated after growing X-ray quality crystals *via* slow evaporation of concentrated CH₂Cl₂ solutions (Fig. 5) and facilitated comparison to previously reported analogues. The N–C–N bond angles measured in the solid state structures of **13** and **14** (120.5(2) and 121.9(3)°, respectively) as well as **15** and **16** (122.2(5) and 122.4(2)°, respectively) were similar, and comparable to those found for analogous complexes containing acyclic diaminocarbene ligands ((ADC)Ir(COD)Cl: 118.9(4)–119.1(4)° and (ADC)Ir(CO)₂Cl: 120.4(2)–122.2(2)°).⁴⁹ Likewise, the Ir–C1 atom distances measured in the solid state structures of **13** and **14** (2.068(2) Å and 2.068(3) Å, respectively) were nearly identical and within the range previously reported for Ir(COD)Cl complexes supported by analogous NHCs and ADCs (2.041(3)–2.090(13) Å).^{27d,50} Additionally, the Ir–C1 distances measured for **15** and **16** (2.112(6) and 2.121(3) Å²⁰) were comparable to analogous complexes containing NHCs or ADCs (2.071(4)–2.121(14) Å).^{27d,50} Collectively, the structural similarities found in the Ir complexes supported by **1** or **5** suggested to us that the N-substituents bestowed similar steric influences on the coordinated metal centers.

**Fig. 5** Top: ORTEP diagram of **13** showing ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Key atom distances (Å) and angles (°): Ir–C1, 2.068(2); N1–C1–N2, 120.5(2). Bottom: ORTEP diagram of **15** showing ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Key atom distances (Å) and angles (°): Ir–C1, 2.112(6); N1–C1–N2, 122.2(5).

To quantify the steric properties of **5**, the buried volume (%V_{Bur}), which provides the volume occupied by ligand atoms within a sphere centered on the metal, was calculated from the solid state structure of **13** using the method reported by Cavallo.⁵¹ The %V_{Bur} calculated for **5** (28.4) was smaller than that reported for **1** (30.2)²⁰ as well as *N,N'*-dimesityl-*N,N'*-dimethylformamidin-2-ylidene (29.8; structure not shown).⁴⁹ Collectively, these results were encouraging as the aforementioned ADC had been successfully incorporated into stable Ru-based olefin metathesis catalysts.^{43b}

We next investigated the electrochemical properties of **13** and **15** to evaluate the degree of electronic communication between the Fe and Ir centers. The CV recorded for **13** in CH₂Cl₂ exhibited two reversible oxidations at $E_{1/2}$ = 0.81 and 1.02 V *versus* SCE, which were assigned to the Fe and Ir metal centers, respectively (Table 1; see also Fig. S5†). These values were comparable to those previously reported for **14** ($E_{1/2}$ = 0.76 and 1.02 V),²⁰ although the Ir centered oxidation measured for **13** occurred at a potential higher than those recorded for other Ir(COD)Cl complexes supported by NHCs ($E_{1/2}$ = 0.65–0.97 V).^{20,27c,52} Upon ligand exchange of the cyclooctadiene ligand for two π -acidic CO ligands (*i.e.*, **15**), a significant anodic shift was observed in the redox couple attributed to the Fe center ($E_{1/2}$ = 0.96 V, $\Delta E_{1/2}$ = 150 mV) and the Ir oxidation process was no longer observed within the solvent window (see Fig. S6†), consistent with our prior report for the oxidation of **14** *versus* **16** ($\Delta E_{1/2}$ = 180 mV) and related complexes.^{20,22,52,53} The 150 mV shift observed upon ligand exchange (*i.e.*, **13** → **15**) suggested to us that the electronic communication

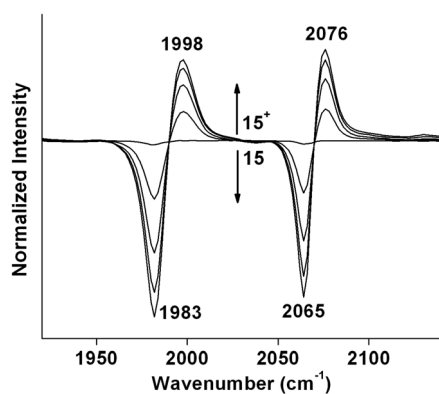


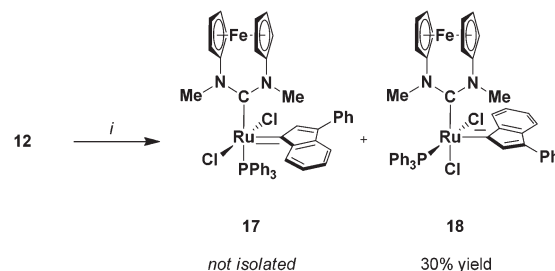
Fig. 6 FT-IR difference spectra collected over time in CH_2Cl_2 showing the disappearance of **15** (1985 and 2065 cm^{-1}) with concomitant formation of **15**⁺ (1998 and 2076 cm^{-1}) upon oxidation (applied voltage = +1.2 V). The arrows indicate the direction of the spectral changes over time.

between the Ir and Fe centers was significant and that the decrease of electron density on the Ir center was due to the π -acidic CO ligands, which consequently raised the oxidation potential of the ferrocene moiety.

The degree of electronic communication between the FcDAC ligand and the Ir center in **15** was also investigated using a spectroelectrochemical FT-IR analysis (Fig. 6). Applying a potential of 1.2 V to a CH_2Cl_2 solution of **15** resulted in a decrease in the intensities of the signals associated with the starting material (1983 and 2065 cm^{-1}) and were accompanied with the appearance of new absorbances at higher frequencies (1998 and 2076 cm^{-1}), consistent with the formation of **15**⁺. The spectroscopic shift reflected the formation of stronger CO bonds due to decreased π -backbonding from the Ir center resulting from a decrease in σ -donation from **5** upon oxidation.²⁰ To quantify the ligand donating abilities of **5** and **5**⁺, the aforementioned ν_{CO} s were converted to their corresponding the Tolman electronic parameters (TEPs)⁵⁴ using Nolan's modification^{27d} of Crabtree's^{27a} method.⁵⁵ In its neutral form, the TEP for **5** in **15** was calculated to be 2050 cm^{-1} ; upon oxidation, the value shifted by 11 cm^{-1} to 2061 cm^{-1} . For comparison, the TEP of **5** in its neutral form is similar to that of strongly donating *N,N'*-diadamantylimidazolyldiene (TEP = 2049.5 cm^{-1})^{27d} but weakens to that of triethylphosphine (TEP = 2061.7 cm^{-1})^{27d} upon oxidation. Given that the activities displayed by Ru-based olefin metathesis catalysts are strongly dependent on the donating abilities of their ligands,^{24,28g,56} we anticipated that the activity displayed by an olefin metathesis catalyst supported by **5** would depend on the oxidation state of the redox-active FcDAC ligand.

Synthesis of Ru complexes containing **5**

Upon verifying that the electronic communication between **5** and the coordinated Ir center was significant, efforts shifted toward synthesizing Ru alkylidenes thereof.⁵⁷ Given its relative stability compared to analogous Ru-benzylidenes,^{40b} efforts were directed toward accessing a Ru-indenylidene complex. The addition of bis-phosphine Ru-indenylidene **9** to a C_6D_6



Scheme 3 Synthesis of Ru complexes containing **5**. (i) (a) NaHMDS (1.0 equiv.), toluene, rt, 5 min. (b) **9** (0.60 equiv.), toluene, rt, 1 h.

solution of the diaminocarbene **5** (formed *in situ*) appeared to form a mixture of two new products by NMR spectroscopy. For example, diagnostic signals were observed at 9.18 (d, $J = 7.2$, $\alpha\text{-CH}_{\text{indenylidene}}$) and 32.65 ppm (PPh_3) in the corresponding ^1H and ^{31}P NMR spectra (C_6D_6), respectively, of the crude reaction mixture, in addition to the formation of free PPh_3 . These signals were similar to those reported for analogous NHC-containing Ru-indenylidene complexes (^1H NMR: 8.31–7.01 (d, $J = 7.7$ –7.2) and ^{31}P NMR: 30.51–27.3 ppm)^{38,40e,g} and thus were tentatively attributed to the formation of the desired FcDAC indenylidene complex **17** (Scheme 3). Signals assigned to a second product were also observed at δ 10.47 (d, $J = 7.6$, $\alpha\text{-CH}_{\text{indenylidene}}$) and 47.07 ppm. Over time, the mixture of products changed and the latter appeared to be favored.⁵⁸ Isolation of the major product (**18**) *via* column chromatography followed by ^{13}C NMR analysis (CD_2Cl_2) indicated that the complex adopted an unexpected geometry.⁵⁹ For example, doublets assigned to the $\text{C}_{\text{indenylidene}}$ (297.1 ppm, $J = 16.1$ Hz) and $\text{C}_{\text{diaminocarbene}}$ (215.7 ppm, $J = 8.3$ Hz) nuclei, respectively, were observed and accompanied with corresponding $J_{\text{C-P}}$ coupling constants. Collectively, these spectroscopic data suggested to us that the complex adopted a geometry in which the NHC was *cis* with respect to the phosphine nucleus rather than the commonly observed *trans* relationship (*cf.*, **17**).^{40m,59,60} Additional support for the aforementioned structural assignment was gleaned from a single crystal X-ray diffraction analysis. X-ray quality crystals were obtained by vapor diffusion of hexanes into a saturated benzene solution, which revealed that the phosphine and diaminocarbene were indeed oriented in a *cis* fashion (Fig. 7).

Preliminary assessment of the catalytic activities displayed by FcDAC-Ru complexes

After the synthesis and characterization of **18**, a preliminary investigation of its ability to catalyze the ring-closing metathesis (RCM) of diethyl diallylmalonate (DDM) and the ring-opening metathesis polymerization (ROMP) of COD was conducted. Although catalytic activity was not observed under the standardized conditions reported by Grubbs and co-workers (CD_2Cl_2 , 30 $^\circ\text{C}$),⁶¹ enhanced activities were observed at 80 $^\circ\text{C}$ in toluene. For example, the RCM of DDM reached 20% conversion after 1 h ($[\text{DDM}]_0 = 0.1$ M, $[\text{18}]_0 = 1$ mol%) and quantitative

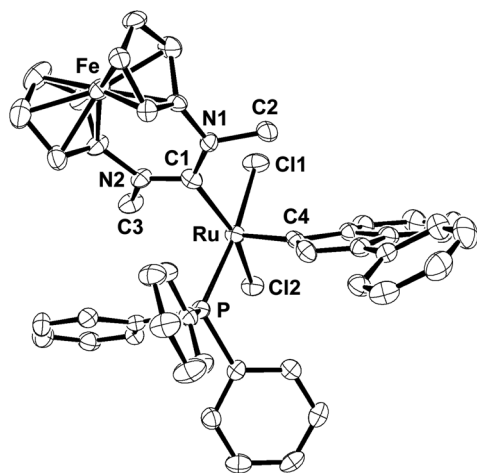


Fig. 7 Left: ORTEP diagram of **18** showing ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Key atom distances (Å) and angles (°): Ru–C1, 2.063(3); Ru–C2, 1.862(4); Ru–P, 2.331(1); N1–C1, 1.358(5); N1–C2, 1.354(5); N1–C1–Ru, 111.4(2); N2–C1–Ru, 127.6(2); C1–Ru–C2, 102.2(1); C1–Ru–P, 97.9(1); Cl1–Ru–Cl2, 87.98(3); N1–C1–N2, 120.8(2).

formation of poly(1,4-butadiene) was obtained from COD in less than 1 h ($[\text{COD}]_0 = 0.5 \text{ M}$, $[\mathbf{18}]_0 = 0.1 \text{ mol\%}$).

Evaluation of the electrochemical properties of **18**

Having established that **18** showed high activity toward the ROMP of COD at elevated temperatures, efforts shifted toward evaluating the redox-switchable characteristics of the complex. These efforts required a detailed examination of the electrochemical processes associated with the Fe and Ru centers present in **18**. As shown in Fig. 8A, the cyclic voltammogram recorded for **18** in CH_2Cl_2 revealed two nearly overlapping quasi-reversible redox processes ($E_{\text{pa}} = 0.79$ and 0.98 V ; Table 1). To assist with signal assignments, the differential pulse voltammogram (DPV) of **18** was recorded and compared to that obtained for the bis-phosphine Ru-indenylidene complex **9** (Fig. 8B and 8C, respectively). Deconvolution of the former revealed two overlapping oxidations that were separated by approximately 100 mV. In contrast, only one signal was obtained upon deconvolution of the DPV for **9**, which was expected as this complex contains one redox-active metal center. We surmised that the oxidation of the Fe center in **18** occurred at a lower potential than the Ru center based on a comparison to other Ru complexes containing ferrocene moieties.⁶² Moreover, upon oxidation of the ferrocene unit, the Ru center should experience a decrease in electron density due to the introduction of positive charge.^{20,62} Indeed, the redox couple attributed to the Ru center in **18**⁺ ($E_{1/2} = 0.98 \text{ V}$) occurred at a significantly higher potential than those recorded for other Ru-benzylidene⁶³ ($E_{1/2} = 0.45\text{--}0.54 \text{ V}$) and Ru-indenylidene^{40j} ($E_{1/2} = 0.46\text{--}0.67 \text{ V}$) complexes supported by NHCs.

Evaluation of **18** and **18**⁺ by UV/vis and EPR spectroscopy

To support the relative Fe and Ru oxidation assignments, efforts were directed toward evaluating the oxidized product of

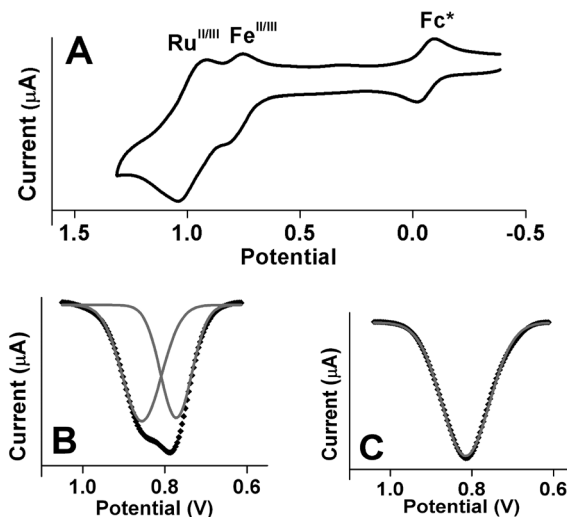


Fig. 8 (A) CV of **18** in CH_2Cl_2 showing the quasi-reversible redox-processes attributed to the Fe and Ru centers. Conditions: 1 mM analyte, 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte, and Fc^* as an internal standard. (B) DPV of **18** (black markers) and deconvolution of the signal (gray line). (C) DPV of **9** (black markers) and deconvolution of the signal (gray line). Conditions for (B) and (C): CH_2Cl_2 solution containing 1 mM analyte and 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte, 4 mV increment, 50 mV amplitude, 0.1 s pulse width, 0.0167 s sample width, 1 s pulse period.

18 using UV/vis and EPR spectroscopy. Previous reports have shown that the oxidation products obtained by treating ferrocene and ferrocene-substituted derivatives with 2,3-dichloro-5,6-dicyanoquinone (DDQ) ($E_{1/2} = 0.58 \text{ V}$ versus SCE in CH_2Cl_2 – $[\text{Et}_4\text{N}][\text{ClO}_4]$)⁶⁴ may be characterized using the aforementioned techniques.^{64,65} To begin, a CH_2Cl_2 solution of **18** ($[\mathbf{18}]_0 = 0.13 \text{ mM}$) was treated with one equivalent of DDQ.⁶⁶ Subsequent analysis of the resulting solution by UV/vis spectroscopy revealed diagnostic absorption bands attributed to $\text{DDQ}^{\cdot-}$ (Fig. 9A). For example, the absorption bands recorded at $\lambda_{\text{max}} = 582, 542, \text{ and } 347 \text{ nm}$ were comparable to those reported for products obtained *via* the reaction of ferrocene with DDQ ($\lambda_{\text{max}} = 587, 548, \text{ and } 344 \text{ nm}$) and other literature values for the $\text{DDQ}^{\cdot-}$ ion.^{65a,c} Although this result provided evidence that DDQ had been reduced, the strong absorbance in the expected region for ferrocenium (620 nm)^{67,68} prevented unambiguous assignment of an Fe *versus* a Ru based oxidation process.⁶⁹

To determine the identity of the metal center (or centers) undergoing oxidation, the oxidized product of **18** (*i.e.*, **18**⁺) was also studied using EPR spectroscopy. The ferrocenium ion exhibits highly anisotropic *g*-tensors that typically result in a component at approximately $g = 4$.⁷⁰ Conversely, Ru^{III} exhibits broad signals with a relatively small *g*-anisotropy, with individual *g*-values occurring between $g = 1.5$ and $g = 2.5$.⁷¹ X-band EPR spectra of **18** after treatment with DDQ in CH_2Cl_2 were recorded at 110 K (Fig. 9C; see also Fig. S10–S12†). Oxidation of **18** using one or two equivalents of DDQ resulted in nearly identical spectra with two major features observed at $g = 4.29$ and 2.01 . Given its high intensity and relative sharpness, the signal at $g = 2.01$ was assigned to an

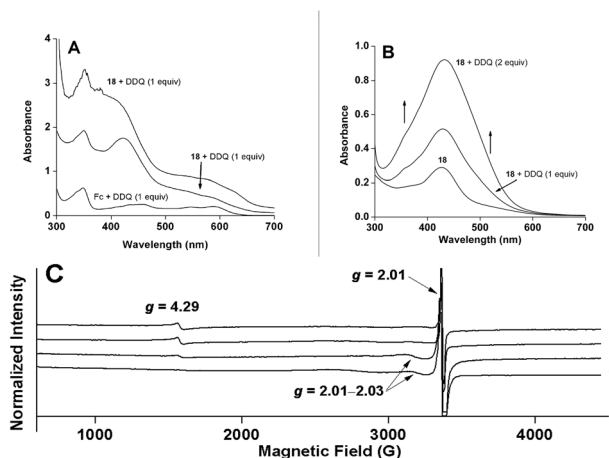


Fig. 9 (A) UV/vis absorption spectra of **18** ([**18**]₀ = 0.13 mM) after treatment with DDQ ([DDQ]₀ = 0.13 mM or 0.26 mM) in CH₂Cl₂ and ferrocene after treatment with DDQ ([ferrocene]₀ = [DDQ]₀ = 0.12 mM). (B) UV/vis absorption spectra of **18** ([**18**]₀ = 75 μM) and **18** ([**18**]₀ = 75 μM) after treatment with DDQ ([DDQ]₀ = 75 μM or 150 μM) in toluene-CH₂Cl₂ (79:1 v/v). (C) X-band EPR spectra. Conditions: 110 K, 9.438 GHz frequency, 100 kHz modulation frequency, and 2.0 mW power. (a) **18** ([**18**]₀ = 1 mM) after treatment with DDQ ([DDQ]₀ = 1 mM) in CH₂Cl₂; (b) **18** ([**18**]₀ = 0.67 mM) after treatment with DDQ ([DDQ]₀ = 1.33 mM) in CH₂Cl₂; (c) **18** ([**18**]₀ = 1 mM) after treatment with DDQ ([DDQ]₀ = 6.6 mM) in toluene; (d) **6** ([**6**]₀ = 1 mM) after treatment with DDQ ([DDQ]₀ = 1 mM) in CH₂Cl₂. See Fig. S10–S15† for individual spectra and additional parameters.

organic-centered radical arising from DDQ^{•−}; the weaker, broad signal at $g = 4.29$ was consistent with that expected from an anisotropic Fe^{III}-centered radical. Since signals could not be attributed to the formation of a Ru^{III} species, the data were consistent with our above assessment that the Fe center oxidized at a lower potential than the Ru center in **18**. The EPR spectrum recorded after treating **18** with DDQ was also studied in toluene, as this solvent was found to facilitate catalytic activity at elevated temperatures. When an excess of DDQ was used (4 equiv. relative to **18**), signals were observed at $g = 4.29$ and 2.01, and assigned to Fe^{III} and semiquinone centered radical species, respectively. In addition, a weak broad signal was present at $g = 2.01$ (overlapping with the organic radical), which was consistent with a Ru-based paramagnetic species. Similar signals ($g = 4.28$ and 2.00) and assignments were reported by Kojima and co-workers for an oxidized Ru^{II} complex containing a ferrocene-substituted pyridylamine ligand.⁷² As a control, an EPR spectrum was recorded in CH₂Cl₂ for **6** (which contains only one metal center) after treatment with DDQ (see ESI†). One strong signal was observed at $g = 2.01$ and assigned to the formation of DDQ^{•−}; additionally, a broad signal attributed to a Ru^{III} species was recorded at $g = 2.03$.^{70b,71}

Redox-switchable ring-opening metathesis polymerizations

Finally, the effect of ligand oxidation on the catalytic activity displayed by **18** was examined. Building on the aforementioned UV/vis and EPR studies, DDQ was selected as an oxidant for **18**. Decamethylferrocene (Fc*) was selected as the reductant on account of its appropriate oxidation potential

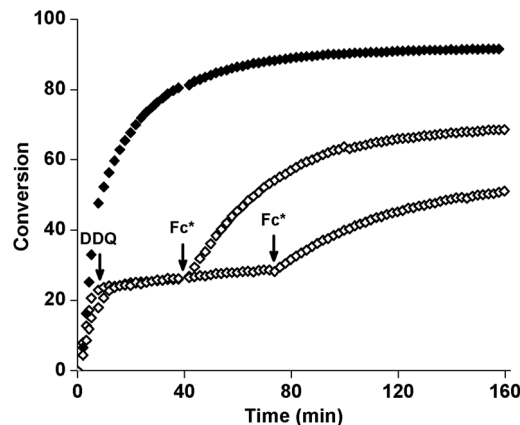


Fig. 10 Redox-switchable ROMP of *cis,cis*-1,5-cyclooctadiene using **18**. All reactions were conducted in toluene-*d*₈/CD₂Cl₂ 79:1 v/v at 60 °C and the corresponding conversions were monitored by ¹H NMR spectroscopy. For the redox-switchable reactions (◇), DDQ (4 equiv. relative to **18**) was added after the conversion had reached approximately 25%. Subsequently, Fc* (5 equiv.) was added after an additional 0.5 h or 1 h. A control reaction where no oxidant or reductant was added over the course of the polymerization was also performed (◆). See main text and Experimental section for additional details.

($E_{1/2} = -0.057$ V in CH₂Cl₂ versus SCE)⁷³ and compatibility with the system under study (*i.e.*, the oxidation product, decamethylferrocenium, was expected to be a spectator ion).⁷³ As summarized in Fig. 10, the ROMP of 1,5-cyclooctadiene ([COD]₀ = 0.5 M) in toluene-CD₂Cl₂ (79:1 v/v)⁷⁴ at 60 °C using **18** as the catalyst (0.04 mol%) was monitored over time by NMR spectroscopy. When the conversion of monomer to polymer had reached approximately 25%, excess DDQ (4 equiv. relative to catalyst) was added,⁷⁵ which significantly reduced the rate constant of the polymerization reaction (pre-oxidation: $k_{\text{obs}} = 0.045$ s^{−1}; post-oxidation: $k_{\text{obs}} = 0.0012$ s^{−1}). Subsequent addition of Fc* (5 equiv. relative to catalyst) after either 30 min or 1 h restored the activity displayed by the catalyst. It appeared that the oxidized catalyst may slowly decompose over time, as the rate constant measured after reducing the catalyst after 1 h was lower than that observed after reduction after 30 min ($k_{\text{obs}} = 0.0066$ s^{−1} versus 0.016 s^{−1}, respectively). The premature catalyst decomposition may be due to the quasi-reversible nature of the Fe oxidation process. Moreover, from the aforementioned UV/vis and EPR studies involving **18**, it is feasible that the Ru center may also undergo oxidation, facilitating decomposition and contributing to the reduced catalytic activity. Regardless, the decreased rate of reaction observed upon the oxidation of **18** was consistent with the weaker ligand donating ability of 5⁺ (*versus* 5) and thus generating a relatively less active catalyst. We believe that the subsequent reduction of the catalyst returned the ligand to its neutral, relatively strongly donating form and restored the catalytic activity intrinsic to **18**.^{28g,56}

To confirm that the aforementioned changes in catalytic activity were driven by redox-induced changes in catalyst electronics rather than by precipitation driven phenomena,^{7a} equimolar solutions of DDQ and **18** were analyzed by UV/vis

spectroscopy in a solution of 79:1 v/v toluene-CH₂Cl₂. As shown in Fig. 9B, increased absorption bands in the 500–600 nm region as well as the shoulder observed at 357 nm were consistent with those observed upon the oxidation of **18** in CH₂Cl₂ (see above). The addition of 2 equiv. of DDQ relative to **18** lead to a further increase in absorbance and no precipitant was evident. Collectively, these observations reinforce the notion that adding an oxidant to the catalyst diminishes the donating ability of the FcDAC ligand rather than altering the solubility of the corresponding catalyst.

Conclusion

In summary, we report that FcDACs may be used as redox-switchable ligands to alter the performance displayed by olefin metathesis catalysts. The formation of various Ru-complexes incorporating *N,N'*-di-iso-butyl FcDAC **1** was observed but proved too difficult to isolate. A synthetic route to *N,N'*-dimethyl FcDAC **5** was developed, and this ligand was studied *via* its Ir(COD)Cl and Ir(CO)₂Cl complexes. Compared to analogous Ir(COD)Cl and Ir(CO)₂Cl complexes incorporating **1**, FcDAC **5** exhibited nearly identical electronic properties but reduced steric bulk. Building on these results, the first examples of Ru-based metathesis catalysts containing FcDAC ligands were synthesized and characterized in solution as well as in the solid state. The oxidation of (5)(PPh₃)Cl₂Ru(3-phenylindenyld-1-ene) (**18**) using DDQ as the oxidant was studied using UV/vis and EPR spectroscopy, which indicated that the oxidation of the FcDAC ligand had occurred preferentially over the Ru center. The ability of **18** to function as a redox-switchable catalyst was then demonstrated in the ROMP of *cis,cis*-1,5-cyclooctadiene. Chemical oxidation of the catalyst using DDQ resulted in a significant decrease in the observed rate of polymerization and subsequent reduction restored catalytic activity. UV/vis spectroscopy indicated that the catalyst was soluble upon oxidation and thus the changes in the observed rates were attributed to the electronic tuning of the Ru center *via* a ligand-centered oxidation process rather than redox-induced precipitation. Collectively, these results underscore the potential of FcDACs to impart redox-switchable functions to transition metal catalysts. Due to the wide and growing applicability of NHC metal complexes in various synthetic processes,⁷⁶ we expect the FcDACs to be useful in outfitting a broad range of catalysts with redox-switchable functions.

Experimental

General considerations

Toluene and CH₂Cl₂ were dried and degassed using a Vacuum Atmospheres Company solvent purification system and then subsequently stored over 3 Å molecular sieves. Benzene-*d*₆ was distilled from sodium and benzophenone ketyl under an atmosphere of nitrogen then degassed by three, consecutive freeze-pump-thaw cycles. CD₂Cl₂ and toluene-*d*₈ (99.9%) were

purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. (PCy₃)₂Cl₂Ru=CHPh (Cy = cyclohexyl) (**6**) was purchased from Aldrich. Diethyl diallylmalonate (DDM) was dried by stirring over 3 Å molecular sieves then degassed by three consecutive freeze-pump-thaw cycles. *cis*, *cis*-1,5-Cyclooctadiene (COD) was distilled from CaH₂ under an atmosphere of N₂ then degassed by three consecutive freeze-pump-thaw cycles. *N,N'*-Di-iso-butylformamidine[3]-ferrocenophane-BF₄ ([**1H**][BF₄]),¹⁹ *N,N'*-diphenylformamidine[3]ferrocenophane-BF₄ ([**2H**][BF₄]),¹⁹ (PPh₃)₂Cl₂Ru(3-phenylindenyld-1-ene),³³ (SImes)(pyridine)₂Cl₂Ru=CHPh⁷⁷ (SImes = 1,3-dimesitylimidazolin-2-ylidene) were synthesized according to literature procedures. Sodium hexamethyldisilazane (NaHMDs) (Acros) was purchased from Fisher Scientific and used as received. All other materials and solvents were of reagent quality and were used as received. Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen using standard drybox or Schlenk techniques.

Instrumentation

¹H and ¹³C {¹H} NMR spectra were recorded using a Varian 300, 400, 500 or 600 MHz spectrometer. Chemical shifts δ (in ppm) were referenced to tetramethylsilane using the residual solvent as an internal standard. For ¹H NMR: CDCl₃, 7.24 ppm; C₆D₆, 7.15 ppm; toluene-*d*₈, 2.09 ppm; CD₂Cl₂, 5.32 ppm; DMSO-*d*₆, 2.49 ppm. For ¹³C NMR: CDCl₃, 77.0 ppm; CD₂Cl₂, 53.8 ppm; DMSO-*d*₆, 39.5 ppm. Coupling constants (*J*) are expressed in hertz (Hz). ³¹P NMR spectra were recorded using a Varian 300 MHz spectrometer, with chemical shifts δ (in ppm) referenced externally to H₃PO₄. X-band EPR spectra were recorded on a Bruker EMX plus spectrometer equipped with a high sensitivity cavity and variable temperature unit accessory. Melting points (m.p.) were determined using a melt-temp apparatus and are uncorrected. Decomposition temperatures (*T*_d) were determined by thermogravimetric analyses (TGA) using a Mettler Toledo TGA/SDTA 851e instrument at a scan rate of 25 °C min⁻¹ under an atmosphere of air. UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer. All measurements were made using matched 6Q Spectrosil quartz cuvettes (Starna) with 1 cm path lengths and 3.0 mL sample solution volumes. Electrochemical experiments were conducted on CH Instruments Electrochemical Workstations (series 630B and 700B) using a gastight, three-electrode cell under an atmosphere of dry nitrogen. The cell was equipped with gold working and tungsten counter electrodes as well as a silver wire quasi-reference electrode. Measurements were performed in dry CH₂Cl₂ with 0.1 M [*n*-Bu₄N][PF₆] as the electrolyte and (Me₅Cp)₂Fe (Fc*) (Cp = cyclopentadienyl) as the internal standard. All potentials were determined at 100 mV s⁻¹ scan rates and were referenced to saturated calomel electrode (SCE) by shifting (Fc*)^{0/+} to -0.057 V (CH₂Cl₂), unless otherwise noted.⁷³ IR spectra were recorded using a Perkin-Elmer Spectrum BX FT-IR instrument. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument (ESI or CI) and are reported as *m/z*

(relative intensity). Elemental analyses were performed by Midwest Microlabs, LLC (Indianapolis, IN).

1,1'-Diformamidoferrocene (10).⁷⁸ A 20 mL glass vial was charged with 1,1'-diaminoferrocene⁷⁹ (1.7 g, 7.9 mmol), phenyl formate (2.1 g, 95%, 17 mmol) and a stir bar. Upon addition of the phenyl formate, the reaction mixture instantly turned dark brown and generated an exotherm. The reaction mixture was subsequently stirred for 4 h at ambient temperature and evaporated to dryness. The crude product was purified *via* column chromatography (media SiO₂, eluent 9 : 1 v/v CH₂Cl₂–MeOH) to afford the desired compound as an orange powder (1.7 g, 80% yield). M.p. 118–120 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.46 (s, 0.4H), 9.34 (s, 1H), 9.25 (m, 0.2H), 9.13 (m, 0.4H), 8.40 (m, 0.55H), 8.07 (m, 1.45H), 4.53 (t, *J* = 1.8, 0.85H), 4.50 (t, *J* = 1.8, 2H), 4.28 (t, *J* = 1.8, 0.3H), 4.24 (t, *J* = 1.8, 0.85H), 4.01 (t, *J* = 1.8, 0.3H), 3.99 (m, 1.6H), 3.91 (t, *J* = 1.8, 2.1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 163.1, 159.4, 159.1, 95.9, 94.5, 94.3, 65.7, 65.4, 65.1, 65.1, 62.0, 61.8, 60.9, 60.6. M.p. 118–120 °C. HRMS: [M⁺] Calcd for C₁₂H₁₂N₂O₂Fe 272.02482; Found 272.02431. Anal. Calcd (%) for C₁₂H₁₂N₂FeN₂O₂: C, 52.97; H, 4.45; N, 10.30; Found: C, 53.20; H, 4.49; N, 10.30.

1,1'-Dimethylaminoferrocene (11). A 250 mL Schlenk flask was charged with lithium aluminum hydride (LiAlH₄) (0.30 g, 9.6 mmol), THF (20 mL) and a stir bar. The mixture was cooled to 0 °C in an ice bath. Under a constant stream of nitrogen, a degassed slurry of 1,1'-diformamidoferrocene (500 mg, 1.8 mmol) in THF (20 mL) was added drop-wise over 30 min *via* syringe. After stirring for an additional 30 min at 0 °C, the flask was fitted with a condenser and refluxed for 1 h. The reaction mixture was then cooled to 0 °C in an ice bath and the excess LiAlH₄ was carefully quenched *via* the dropwise addition of degassed water. Excess water (50 mL) and ether (50 mL) were then added which resulted in the formation of a white precipitate. After the white precipitate was allowed to settle, the ethereal phase was separated under nitrogen and evacuated at 20 millitorr for 24 h to give the desired compound as an oxygen-sensitive orange solid (350 mg, 78% yield). M.p. 68–70 °C. ¹H NMR (400 MHz, C₆D₆): δ 3.84 (t, *J* = 1.8, 4H), 3.72 (t, *J* = 1.8, 4H), 2.73 (s, 6H), 1.73 (br s, 2H). ¹³C NMR (100 MHz, C₆D₆): δ 112.3, 63.2, 55.7, 33.8. HRMS: [M⁺] Calcd for C₁₂H₁₄N₂Fe, 244.06629; Found, 244.06561. Due to its high sensitivity toward oxygen, elemental analysis of this compound was not performed.

***N,N'*-Dimethylformamidinium[3]ferrocenophane BF₄ (12).** 1,1'-Dimethylaminoferrocene (11) (639 mg, 2.61 mmol), degassed trimethylorthoformate (5 mL), tetrafluoroboric acid etherate (0.35 mL, 2.6 mmol) and a stir bar were added to a 25 mL Schlenk flask under nitrogen. The reaction mixture was heated for 30 min at 60 °C. After allowing the mixture to cool to room temperature, the solvent was removed under vacuum. The residue was extracted with CH₂Cl₂ (5 mL) and filtered through a 0.25 μm PTFE filter into hexanes (50 mL) to afford a golden precipitate, which was collected by filtration and washed with additional hexanes (100 mL). The solid was dried under vacuum to afford the desired compound as a gold

powder (780 mg, 88% yield). Crystals suitable for X-ray structure determination were grown by slow diffusion of ether into a saturated CH₂Cl₂ solution of the compound. *T*_d 305 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.71 (s, 1H), 4.67 (t, *J* = 1.8, 4H), 4.45 (t, *J* = 1.8, 4H), 3.50 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 162.0, 93.7, 71.7, 67.2, 45.7. HRMS: [M⁺ – BF₄] Calcd for C₁₃H₁₅N₂Fe 255.0575; Found 255.05792. Anal. Calcd (%) for C₁₃H₁₅N₂FeBF₄: C, 45.67; H, 4.42; N, 8.19; Found: C, 45.43; H, 4.42; N, 8.08.

(*N,N'*-Dimethyldiaminocarbene[3]ferrocenophane)Ir(COD)Cl (13). A 7.5 mL glass vial equipped with a stir bar was charged with 12 (74 mg, 0.22 mmol), NaHMDs (98%, 42 mg, 0.22 mmol) and toluene (3 mL). The mixture was then stirred for 5 min. [Ir(COD)Cl]₂ (72 mg, 0.12 mmol) was added, and the resulting brown mixture was stirred for 12 h, after which point the work up was performed in air. The solvent was removed by evaporation under reduced pressure. The residue was taken up in a minimal amount of CH₂Cl₂ and purified using column chromatography (media SiO₂, eluent 3 : 1 v/v hexanes–ethyl acetate, *R*_f = 0.18). The yellow fraction was collected and the solvent was removed by evaporation under reduced pressure to give the desired product as a yellow powder (70 mg, 55% yield). ¹H NMR (400 MHz, CDCl₃): δ 4.47 (m, 2H), 4.18 (m, 12H), 3.91 (m, 2H), 2.96 (m, 2H), 2.20 (m, 4H), 1.75–1.50 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 215.6, 100.2, 81.4, 71.0, 70.9, 66.3, 65.5, 53.2, 48.8, 33.1, 29.4. HRMS: [M⁺ – 2H – Cl] Calcd for C₂₁H₂₄N₂FeIr 553.09180; Found 553.09146. Anal. Calcd (%) for C₂₁H₂₆ClN₂FeIr: C, 42.75; H, 4.36; N, 4.94; Found: C, 42.87; H, 4.65; N, 4.65.

(*N,N'*-Dimethyldiaminocarbene[3]ferrocenophane)Ir(CO)₂Cl (15). A 20 mL glass vial equipped with a stir bar was charged with 13 (70 mg, 0.12 mmol) and CH₂Cl₂ (5 mL), and then sealed with a septum. The solution was then stirred under an atmosphere of CO (1 atm) for 3 h. The solvent was removed by evaporation under reduced pressure to give a yellow powder. Subsequent washing of the powder with a minimal amount of pentane followed by drying under vacuum for 48 h to remove the residual 1,5-cyclooctadiene afforded the desired product as a yellow solid (51 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃): δ 4.27 (m, 4H), 4.23 (m, 2H), 4.16 (m, 2H), 3.98 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 206.2, 180.5, 168.5, 99.4, 71.6, 71.5, 66.1, 65.6, 50.0. FT-IR (CH₂Cl₂): 2065, 1983 cm^{–1}. HRMS: [M⁺ – 2H – Cl] Calcd for C₁₅H₁₄N₂O₂FeIr 503.0034, Found 503.0029. Anal. Calcd (%) for C₁₅H₁₆ClN₂O₂FeIr: C, 33.37; H, 2.99; N, 5.19; Found: C, 33.84; H, 2.60; N, 5.00.

(*N,N'*-Dimethyldiaminocarbene[3]ferrocenophane)(PPh₃)Cl₂Ru(3-phenylindenylid-1-ene) (18). A 6 mL glass vial equipped with a stir bar was charged with 12 (103 mg, 0.301 mmol), NaHMDs (57.2 mg, 0.312 mmol) and toluene (6 mL), and then sealed with a Teflon lined cap. The reaction mixture was stirred for 5 min at ambient temperature. (PPh₃)₂Cl₂Ru(3-phenylindenylid-1-ene) (9) (158 mg, 0.178 mmol) was added and the vial was re-sealed with a Teflon lined cap. The solution was stirred at ambient temperature for 1 h and then concentrated under reduced pressure to afford a brown solid. The solid was then purified by column

chromatography (media SiO₂, eluent 10:1 v/v hexanes–ethyl acetate) to elute a light red fraction (17). The solvent was then switched to ethyl acetate to elute a dark red fraction (18). The second dark red fraction was evaporated to dryness by concentration under reduced pressure. Benzene was then added (3 mL) which caused a red solid to precipitate upon standing. The solid was recovered by vacuum filtration to yield the desired complex as a red microcrystalline solid (18.9 mg, 12% yield). The solvent was then removed from the first fraction by evaporation under reduced pressure. Subsequent purification of this fraction by chromatography using the aforementioned solvent system increased the overall combined yield of **18** to 30% (46.8 mg). X-ray quality crystals were grown by vapor diffusion of hexanes into a saturated benzene solution of the complex. ¹H NMR (300 MHz, CD₂Cl₂): δ 9.38 (d, 1H, J = 6.9), 7.59–7.25 (m, 23H), 6.13 (s, 1H), 4.35 (m, 2H), 4.26 (br s, 2H), 4.23 (br s, 2H), 4.17 (m, 1H), 4.05 (m, 1H), 3.38 (s, 3H), 2.71 (s, 3H). ¹³C NMR (150 MHz, CD₂Cl₂): δ 297.1 (d, J = 16.1), 215.7 (d, J = 8.3), 145.01, 145.00, 141.8, 140.6, 140.5, 137.9, 135.5, 134.7, 131.5, 130.9, 130.81, 130.80, 130.4, 129.4, 129.1, 128.9, 128.71, 128.67, 128.6, 126.8, 118.3, 100.0, 99.5, 72.3, 72.2, 71.7, 71.5, 67.4, 66.5, 65.4, 64.4, 50.9, 46.9. ³¹P NMR (121 MHz, CD₂Cl₂): δ 47.99. HRMS: [M⁺ – Cl] Calcd for C₄₆H₃₉ClFeN₂Pru 843.09420; Found 843.09268. Anal. Calcd (%) for C₄₆H₃₉Cl₂FeN₂Pru·(1/6)CH₂Cl₂: C, 62.11; H, 4.44; N, 3.14. Found: C, 62.05; H, 4.48; N, 3.07.

General procedure used to measure the kinetics of the ROMP of *cis,cis*-1,5-cyclooctadiene (COD)

Inside a drybox, an NMR tube was charged with either (i) 25 μ L (0.40 μ mol) of a 0.016 M stock solution of catalyst in CD₂Cl₂⁷⁴ and 0.78 mL of CD₂Cl₂ or (ii) 25 μ L (0.40 μ mol) of a 0.016 M stock solution of catalyst in CD₂Cl₂ and 0.78 mL of toluene-*d*₈. The tube was capped and shaken vigorously before COD (49.1 μ L, 43.3 mg, 0.40 mmol; [monomer]₀ = 0.5 M) was added. The reaction was then removed from the drybox and allowed to proceed at either 30 or 80 °C in an oil bath. After 1 or 24 h, the progress of the reaction was determined by comparing the integral of the signals attributed to the methylene protons of the monomer (δ = 2.17 ppm, m) *versus* the polybutadiene product (δ = 2.08 ppm, br m).

General procedure used to monitor the RCM of diethyl diallylmalonate

Inside a drybox, an NMR tube was charged with either (i) 50 μ L (0.80 μ mol) of a 0.016 M stock solution of catalyst in CD₂Cl₂ and 0.75 mL of CD₂Cl₂ or (ii) 50 μ L (0.80 μ mol) of a 0.016 M stock solution of catalyst in CD₂Cl₂ and 0.75 mL of toluene-*d*₈. The tube was then capped and shaken vigorously before DDM (19.3 μ L, 19.2 mg, 0.080 mmol; [DDM]₀ = 0.1 M) was added. The tube was then re-capped, shaken, and sealed with parafilm. The reaction was then removed from the drybox and allowed to proceed at either 30 or 80 °C in an oil bath. After 1 or 24 h, the progress of the reaction was determined by comparing the integral of

the signals attributed to the methylene protons in DDM (δ = 2.61 ppm) with those found in the product (δ = 2.98 ppm).

General procedure used to measure the kinetics of the redox-switchable ROMP of *cis,cis*-1,5-cyclooctadiene (COD)

In a nitrogen filled drybox, a stock solution of **18** in CD₂Cl₂ was prepared (0.016 M). Stock solutions of DDQ (0.02 M) and Fe* (0.02 M) were separately prepared in toluene-*d*₈. A screw-cap NMR tube was then charged with catalyst stock solution (10 μ L, 0.16 μ mol) and toluene-*d*₈ (0.79 mL), and then sealed with a septum-top screw-cap. The NMR tube was then equilibrated to 60 °C inside of an NMR spectrometer. The sample was ejected and COD (49.1 μ L, 43.3 mg, 0.40 mmol; [COD]₀ = 0.5 M) was quickly added through the septum *via* microsyringe. NMR spectra were collected at 2 min intervals until the conversion had reached approximately 25%. The sample was again ejected and DDQ (32 μ L, 0.64 μ mol) was quickly added through the septum top *via* microsyringe. Data acquisition resumed at 2 min intervals until either 30 min or 1 h had elapsed. At this point, the sample was again ejected and Fe* (40 μ L, 80 μ mol) was quickly added through the septum top *via* microsyringe. An NMR array function was then used to record a spectrum every 2 min for 3 h.

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- 58 Conditions which favored the formation of exclusively one product could not be found. After extended reaction times (12 h) at ambient temperature, the final molar ratio of **17** to **18** was approximately 1 : 5.
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